Journal of Thermal Analysis and Calorimetry, Vol. 61 (2000) 243–247

THERMAL DECOMPOSITION STUDIES OF MIXED RARE EARTH HYDROGEN SELENITE CRYSTALS

P. P. Pradyumnan[1*] *and M. A. Ittyachen*[2]

[1]Department of Physics, University of Calicut, Calicut University P.O. Box 673 635
[2]School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam, Kerala, 686 560 India

(Received July 7, 1999; in revised form November 16, 1999)

Abstract

Mixed rare earth hydrogen selenite crystals, neodymium praseodymium hydrogen selenite ($Nd_xPr_{1-x}(HSeO_3)(SeO_3)\cdot 2H_2O$), Neodymium samarium hydrogen selenite ($Nd_xSm_{1-x}(HSeO_3)(SeO_3)\cdot 2H_2O$) and praseodymium samarium hydrogen selenite ($Pr_xSm_{1-x}(HSeO_3)(SeO_3)\cdot 2H_2O$) were prepared by gel diffusion technique. Simultaneous thermogravimetric and differential thermal analysis were carried out on the grown crystals. Decomposition is observed to occurs in six steps, which gives the evidence of successive losses of H_2O and SeO_2. The final product due to decomposition is a mixed rare earth oxides. FT-IR spectrum of the crystal samples heated at different temperatures complemented to the TG-DTA results.

Keywords: FT-IR, rare earth hydrogen selenites, TG-DTA

Introduction

Investigations on the thermal degradation of several rare earth selenite compounds have been described in the literature [1–6]. Even though very little work has been reported on rare earth hydrogen selenite crystals [3]. However no information is available in the literature concerning the thermal degradation of lanthanide double hydrogen selenites.

This paper reports the results of thermal decomposition of mixed rare earth hydrogen selenite crystals. The studied crystals are neodymium praseodymium hydrogen selenite (NPHS), neodymium samarium hydrogen selenite (NSHS) and praseodymium samarium hydrogen selenite (PSHS). All these crystals were grown by gel diffusion technique of rare earth ions. The rare earth hydrogen selenite crystals were characterized by conventional experimental techniques like X-ray, UV-visible and IR etc. [7].

Experimental

The growth of NPHS, NSHS and PSHS crystals were achieved by controlled diffusion of the reactants through the silica gel. Recently a number of investigators have

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[*] Author for correspondence: e-mail: ppp@unical.ac.in.

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

grown rare earth mixed oxalates and tartarates [9–12]. The gel solution was prepared by dissolving SMS in doubly distilled water, adjusting the density to 1.03 gm cc^{-1}. Selenous acid solution (lower reactant) of 1 M concentration was triturated with the gel solution to the desired pH value. The resulting solution was then poured into the crystalliser for gelling. It is found that, gelling take place within 24 h. The respective nitrate (upper reactant) solutions of the required concentration and proportions are poured slowly along the sides of the tube containing the pre-set gel of desired age. Slow diffusion of upper reactant through the gel result in the growth of the crystal. The good quality crystals are taken from the gel and cleaned and dried. The chemical formula of the crystals are, $Nd_{1-1x}Pr_x(HSeO_3)(SeO_3)\cdot 2H_2O$, $Nd_{1-x}Sm_x(HSeO_3)(SeO_3)\cdot 2H_2O$, $Pr_{1-x}Sm_x(HSeO_3)(SeO_3)\cdot 2H_2O$. The thermogravimetric and differential thermal analysis were performed by using SETARAM TGDTA92 instrument in the atmosphere of argon and oxygen from 298 to 1473 K Standard platinum crucible were employed as sample holder and heating rate was 10°C min^{-1} and the sample mass was 100 mg.

Results and discussion

Thermal decompositions of NPHS, NSHS and PSHS were examined thoroughly and occurred in six steps in between 343 to 1473 K depending on the constituent rare earth elements. It is worth noting that the thermal behaviour of these crystals are identical and proceeds by successive decomposition of H_2O and SeO_2 molecules. Tables 1 to 3 presents the analytical data of the crystals. In the simultaneous TG and DTA curves (Figs 1 and 2), mass loss observed up to 550 K, corresponding endothermic peaks and this may be due to hydration of water. The calculated and observed values after degradation tallied with the proposed molecular formula (Tables 1–3). The functional groups were characterized with the IR absorption spectrum of the samples heated for different temperatures (Fig. 3). Table 4 gives the characteristic peaks of the functional groups present in the IR spectrum of the crystals.

Table 1 Thermal degradation of NPHS crystals

DTA range of mass loss	TG range of mass loss	Mass loss obs.	Mass loss calc.
°C		%	
175	135–195	2.1	2.08
250	235–325	8.2	8.48
*388	325–475	6.1	6.11
540	475–585	7.4	7.68
850	585–904	32	33.31
1182	9041–1200	22	24.1

Table 2 Thermal degradation of NSHS crystals

DTA range of mass loss	TG range of mass loss	Mass loss obs.	Mass loss calc.
°C		%	
180	145–245	2.2	2.05
265	245–300	8.0	8.3
*395	300–450	7.8	7.05
565	450–620	10.0	10.15
830	620–900	24.8	24.64
1150	900–1200	34.00	34.84

Table 3 Thermal degradation of PSHS crystals

DTA range of mass loss	TG range of mass loss	Mass loss obs.	Mass loss calc.
°C		%	
170	125–200	2.5	2.06
265	200–300	8.2	8.40
*375	300–420	7.0	7.40
555	420–600	7.6	7.69
840	600–900	32	33
1160	900–1200	20.5	20

Table 4 Spectral data and band assignments of rare earth hydrogen selenite crystals

IR($\bar{\nu}$)	Assignments
473 s	$\nu_2(SeO_3^{2-})$
493 s	ν(Se–O)
670 s	δ(Se–OH)
700 s	$\nu_1(HSeO_3^{2-})$
755 s	ν_3(Se–O)
820 m	$\nu_1(SeO_3^{2-})$
843 m	$\nu_1(HSeO_3^{-})$
1227 s	δ(O–Se–OH)
1640 w	δ(O–Se–OH)
2406 s	ν(OH)
3447 w	ν(OH)

The DTA curves of the three crystals show five endothermic peaks in accordance with the mass loss shown in TG curve except for the decomposition of RR_1SeO_{11}, that is an exothermic peak (the temperature region showing * signs in the Table). This peak can be regarded as the elimination of SeO_2 and simultaneous crystallographic transformation. The thermal decomposition of all the stages can be depicted as

$$2[RR_1(HSeO_3)(SeO_3)\cdot 2H_2O]–1H_2O \rightarrow RR_1Se_4O_{11}\cdot 4H_2O–4H_2O \rightarrow$$

$$\rightarrow RR_1Se_4O_{11}–1/2SeO \rightarrow 1/2[4RR_1Se_7O_{20}]–1/2SeO_2 \rightarrow RR_1Se_3O_9–2SeO_2 \rightarrow$$

$$\rightarrow RR_1SeO_3–1SeO_2 \rightarrow RR_1O_3$$

where R and R_1 are the constituent rare earth elements.

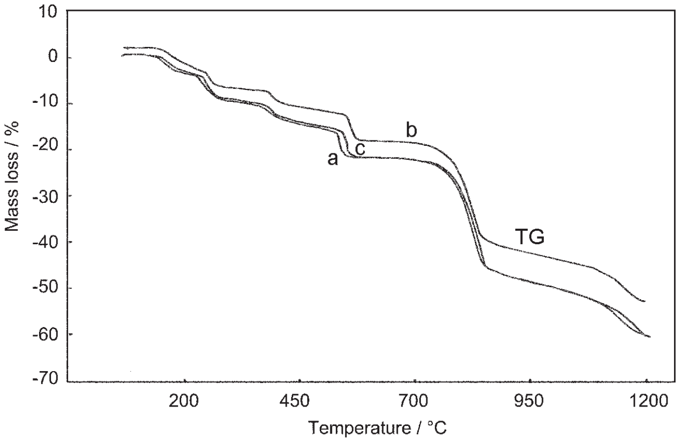

Fig. 1 Thermogravimetric curve of mixed rare earth selenites a – for NPHS crystal, b – for NSHS crystal, c – for PSHS crystal

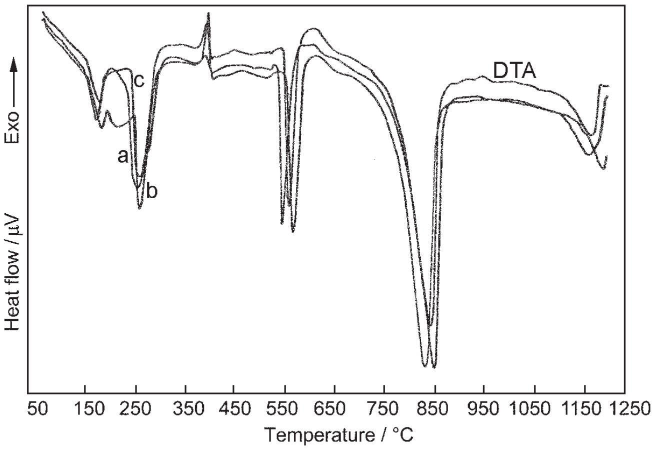

Fig. 2 DTA curve of mixed rare earth selenites a – for NPHS crystal, b – for NSHS crystal, c – for PSHS crystal

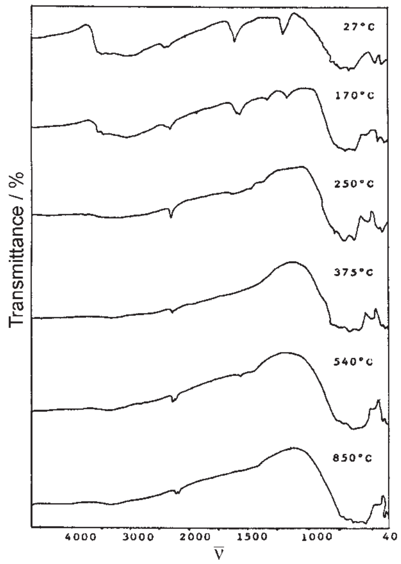

Fig. 3 The FT-IR spectra of mixed rare earth hydrogen selenite (NPHS) crystals heated at different temperatures (1) at 27, (2) 170, (3) 250, (4) 375, (5) 540, (6) 850°C

Conclusions

The decomposition curves of NPHS, NSHS, PSHS are identical in nature and it is in good agreement with that single selenite crystals [8]. The proposed chemical formula and IR spectra of these crystals are matched with each other [8]. As in the case of rare earth oxalates [13] we propose that these crystals can be used as precursor for the preparation of the corresponding superconducting oxides.

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